Electronic Nose Technology: Today's Big Challenge

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Abstract

Electronic nose devices have got attention in the field of sensor technology during the past twenty years, largely because of the discovery of various applications derived from research in diverse fields of applied sciences. Recent applications of electronic nose technologies have come through advances in sensor design, material improvements, software innovations and progress in micro circuitry design and systems integration. The study of many new e-nose sensor types and arrays which are based on different detection principles and mechanism, is closely correlated with the expansion of new applications. Electronic noses have provided a plethora of benefits to a variety of commercial industries, including the agricultural, biomedical, cosmetics, environmental, food, processing, pharmaceutical, military, regulatory, and various scientific research arenas. Advances have improved product attributes, uniformity and consistency as a result of increases in quality control abilities afforded by electronic-nose auditing of all phases of industrial manufacturing processes. This paper is a review of the major electronic-nose technologies, developed since this specialized area was born and became prominent in the mid 1980s, and a depiction of some of the more important and useful applications that have been of greatest profit to human.

Keyword: Electronic Nose, ANN, Biological Olfaction, Headspace Sampling Unit, Gas Sensor Array.

1. Introduction

An electronic nose is an array of non-specific chemical sensors, monitored and analyzed electronically, which mimics the act of the mammalian nose by recognizing patterns of response to vapors. The sensors which are used here are conduct metric chemical sensors which changes resistance when exposed to vapors. The sensors are not particular to any one vapor; it is in the use of an array of sensors, each with a different sensing medium, that gases and gas mixtures can be recognized by the pattern of response of the array. An electronic nose (e-nose) is a device that identifies the specific components of an odor and analyzes its chemical overlay to identify it. An electronic nose includes of a mechanism for chemical detection, such as an array of electronic sensors, and a mechanism for pattern identification, such as a neural network. Electronic noses have been around for several years but have typically been large and costly. Current research is based on making the devices smaller, less expensive, and more sensitive. The smallest version, a nose-on-a-chip is a single computer chip consisting both the sensors and the processing components. An odor is made of molecules, each of which has a specific size and shape. Each of these molecules has a correspondingly sized and shaped receptor in the human nose. When a particular receptor receives a molecule, it sends a signal to the brain and the brain identifies the smell associated with that specific molecule. Electronic noses based on the Biological model work in a same manner, substituting sensors for the receptors, and transmitting the signal to a program for analyzing, rather than to the brain. Electronic noses are one example of a developed research area called biomimetic, or bio mimicry, which involves human-made applications structured on natural Phenomena. Electronic noses were basically used for quality control applications in the food, beverage and cosmetics industries. Current applications include detection of odors specific to diseases for medical diagnosis, and detection of pollutants and gas leaks for environmental protection.

2. Principles of Biological Olfaction

One of the incredible natural systems is the mammalian olfactory system. A special tissue in the nose called olfactory epithelium, consist of olfactory receptor cells. These nerve cells communicate with the odorant molecules and thereby causing

Fig1: Electronic nose prototype

the sensation of smell (Craven 1996, Bartlett 1997b, Pearce 1997). The olfactory cell is a combination of number of cilia, where G receptor binding proteins are situated at the surface of the cilia. These G receptor binding proteins results in excitation in the neurons.

They have moderately overlapping sensitivities to odorants and are about 100 million olfactory cells, which speed up the signal and generate secondary messages (Gardner 1994). Thus the sensory cells in the epithelium react partially by transmitting signals along axon in the olfactory bulb, where it ends in a cluster of neural network called glomeruli. These signals are further processed in about 100000 mitral cells and then finally sent via a granular cell layer to the brain (Keller 1999). In the brain, the signals are decoded using a kind of pattern recognition[1].

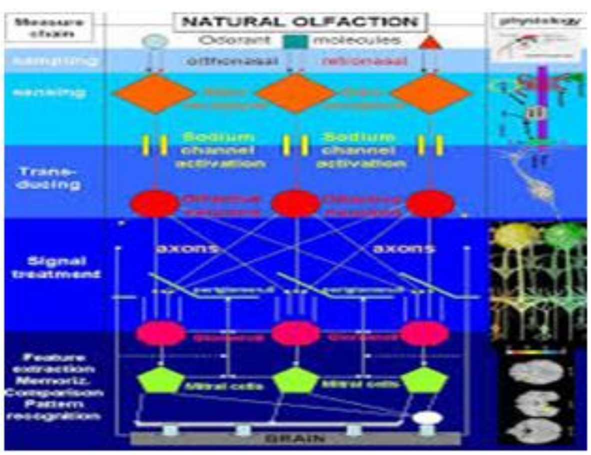

Fig.2: Natural Olfaction

3. Principle of artificial olfactory system

An electronic nose that uses an array of 32 polymer–carbon black composite sensors has been developed, trained, and tested. By choosing a variety of chemical functionalities in the polymers used to make sensors, it is possible to design an array capable of recognizing and quantifying a wide range of target compounds, such as alcohols and aromatics, and differentiating isomers and enantiomers (mirror-image isomers). A model of the interaction between target molecules and the polymer–carbon black composite sensors is still under development to aid in choosing the array members and to enable verification of compounds with reactions not stored in the analysis library. The electronic nose was developed in order to copy human olfaction that acts as a non-seperative techniques: i.e. an odor / flavor is taken as a global fingerprint. Electronic Noses include three major parts: a sample delivery system, a detection system, a computing system. The sample delivery system facilitates the generation of the headspace (volatile compounds) of a sample, which is the fraction analyzed. The system then pushes this headspace into the diagnosis system of the electronic nose. The sample delivery system is necessary to guarantee constant operating conditions. The detection system, which consists of a sensor set, is the "reactive" part of the instrument. When in contact with volatile compounds, the sensors react, which means they experience a change of electrical properties. Each sensor is sensitive to all elusive molecules but each in their specific way. Most electronic noses use sensor-arrays that react to elusive compounds on contact: the adsorption of elusive compounds on the sensor surface causes physical changes of the sensor. A particular response is recorded by the electronic interface transforming the signal into a digital dataset. Recorded datasets are then calculated based on statistical models. The more commonly used sensors include metal oxide semiconductors (MOS), conducting polymers (CP), quartz crystal microbalance, surface acoustic wave (SAW), and field effect transistors (MOSFET).In recent years, other kinds of electronic noses have been developed that utilize mass spectrometry or ultra-fast gas chromatography as a detection system. The computing system works to merge the responses of all of the sensors, which presents the input for the data treatment. This part of the instrument performs global fingerprint test and provides results and presentations that can be easily changed, the electronic nose results can be correlated to those obtained from other techniques (sensory panel, GC, GC/MS).

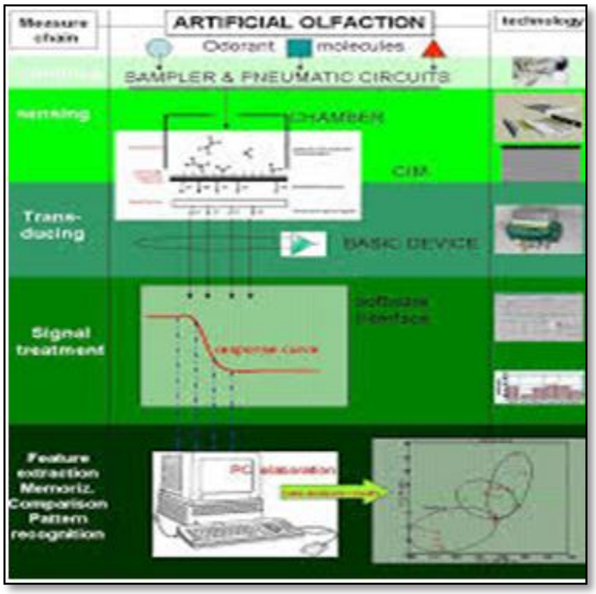

Fig.3: Artificial Olfaction

4. WORKING PRINCIPAL

4.1 Sampling Unit

To detect any substance with an E-nose, the sample has to be brought into the sensor chamber. The role of the sampling unit is to gather the sample, condition it and transfer it into the sensor chamber and then restore the sensor by means of a cleaning technique. The design of the sampling unit should maintain the factors such as temperature, humidity etc which are capable of influencing sensor responses. The factors are kept under required parameters, so that only the configuration of odor is retained in the sample. This type of design of sampling unit ensures good stability, repeatability, fast sensor responses and high amplitude signals. These factors are highly desired, as sampling is the first basic step of data acquisition and hence its execution influences all successive steps. Sample handling techniques can be divided into two main categories: with and without pre concentration depending upon the application and nature of sample (Pearce 2003) if major difference exists between the samples, sampling technique without pre-concentration is sufficient. On the other hand for trace analysis, pre concentration of the sample is needed. For E-nose, there are two techniques to treat the sample of measurement that are headspace sampling and online measurement. The differences in these two strategies are mainly due to a different point of view; in the case of headspace sampling the 'sampling action' is to deliver the sample to the E-nose; in the case of on-line measurement the 'sampling action' is to introduce the E-nose in the sample environment[2].

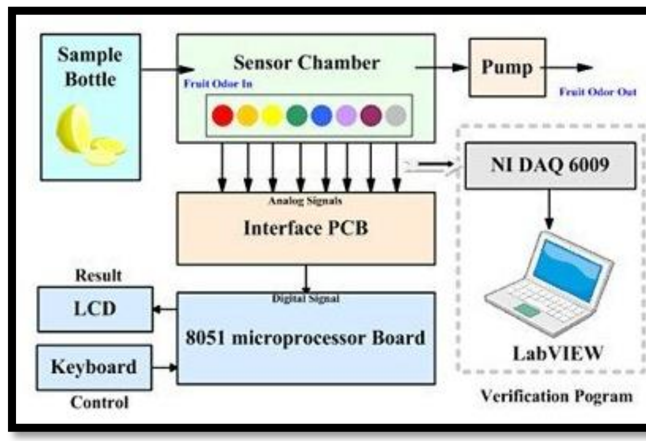

Fig.4: Sampling unit of e nose

4.2 Head Space Sampling

In head space sampling technique, the head space should be sampled with maximum possible efficiency without changing its composition. The Head Space (HS) of a sample consists volatile organic compounds. The measure of head space by the chemical gas sensors exposes the information about the nature and the composition of the sample. This head space or the volume of gas is brought inside the sensor chamber by the sampling unit for further analysis.

A correct and effective application of this technique is obtained with a careful monitoring of partition coefficient (k) and phase ratio (ß). Partition coefficient k, is given by the Equation (1)

$$k=C_i(s)/C_i(g) \qquad (1)$$

where the concentrations of the analyte i in the gas phase is $C_i(g)$ and liquid/solid sample phase is $C_i(s)$.

Compounds that have low k values will tend to partition more readily into the gas phase and have relatively high responses and low limits of detection. Another important parameter to match with the partition coefficient is the phase ratio (ß), defined as the relative volume of the headspace (vg) compared to volume of the sample (vs) in the sample vial.

Lower values for k, ß (i.e., larger sample size) will yield higher responses for volatile compounds (Snow 2002, Iguchi 2000)[3].

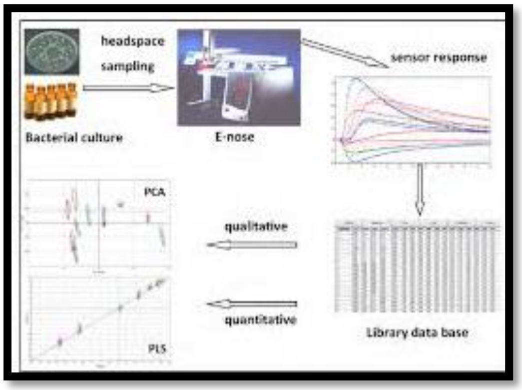

Fig.5: Headspace Sampling Unit

4.3 Online Measurements

The need of online sampling can be due to direct monitoring of particular application. Some major on-line measurement methods like diffusion method, permeation method, bubbler method and sampling bags (Ohnishi 1992, Phillips 1997).

GAS SENSOR ARRAY

The gas sensor array is regarded as the main and most vital part of an E-nose as it is similar to the olfactory nerves in the human olfactory system. It consists of an array of gas sensors, where sensors can be described as a device. This device when exposed to a gaseous chemical compound or mixture of chemical compounds, it changes one or more of its physical features. The physical feature may be the mass of the sensor, electrical conductivity, or capacitance which can be measured and quantified directly or indirectly (Harwood 2001). Sensors can be categorized according to their operating principles, each class having various sensitivity and selectivity. The array of sensors is designed by the principle that averts the composition of sensors which produce the similar information by different means, e.g. pH and conductivity. The E-nose system requires multiple sensors so that it can give unique smell print for a particular class of compound and can be distinguished from other sample. If there is any need to screen a particular class of compounds whose exact composition would vary, then a combination of sensors are required. One sensor of which, is sensitive to a particular compound of interest, while the others detect only the functionality of the compound. For example, 2, 4-dinitrophenyl-hydrazine reacts with all ketones and a sensor based on this reaction would give the total concentration of all ketones present in that sample. However, a polypyrolle-based sensor can distinguish between different ketones based on the minor differences in their polarity. A third sensor can use the principle of molecular size to restrict the ketones detection. Combination of these three sensors will provide definitive information on the mixture to which they are exposed (Troy Nagle 1998, Harwood 2001). This is very important as it allows to repeatedly monitoring the sample of interest with real time variations in the concentrations. The sensory array should be designed to have high sensitivity and low selectivity (Gardner 1992). Sensors are allowed to reach equilibrium after making measurement of odor. The resulting response vectors depend on time and represent absolute change in sensor signal with a measured odor (Dickinson 1998)[4].

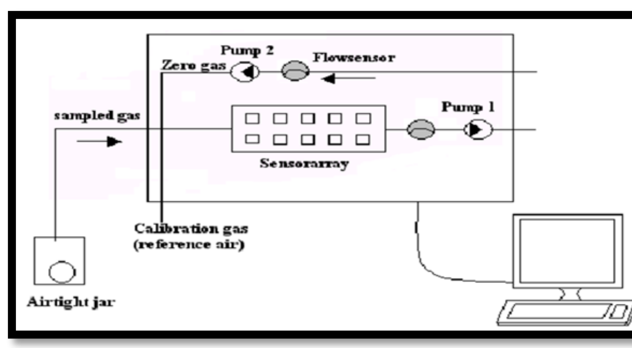

Fig.6: Measurement Of E Nose

4.4 DATA PROCESSING AND PATTERN RECOGNITION UNIT

The multivariate reaction of the sensors can be utilized as an “electronic smell print” to characterize a wide range of elusive compounds by means of pattern identification techniques. Pattern identification may be defined as “the mapping of a pattern results in a given pattern space into a class membership function". It bombards the cross relation and extracts information which is present in the sensor outputs ensemble by feature extraction. The choice of feature can be regarded for subsequent multivariate data analysis. Pre-processing while performing measurements with a multi sensor system like an E-nose, a large amount of dataset is generated. From each sensor more signal parameters can be computed for describing the dynamics of each sensor's reaction to the headspace of the sample. Hence the data extracted from the sensor reacts often have to be pre-processed. Techniques which are used for pre-processing include weighting, standardizing and normalizing of the sensor reaction. Pattern Recognition Methods the term pattern recognition can be defined as the transformation of an input data set, such as sensor signals from an E-nose to an output set of attributes like the type of sample.

The complete pattern recognition consists of two steps: exploration and prediction. In exploration step, the objective is to get an overview of the data by searching the relationship among the measurements and the signals 41 obtained from the sensor and by further recognizing the measurement errors. It is done by explorative and regression methods. The explorative methods allow to 'explore' the sensors' reaction set in a particular application, looking for relationship between these data set and possible existing structure. Regression methods, instead, are devoted to build correlation between an input and output data set. The several explorative and regression methods are Principal Component Analysis (PCA), Principal Component Regression (PCR), Partial Least Squares (PLS) and Multivariate Linear Regression (MLR). In the prediction step, the aim is to find mathematical models of interesting features of the samples. The prediction model can be obtained by soft computing techniques especially by hybrid artificial neural networks. Comparing to the classical methods, Artificial Neural Networks (ANN) are far superior. These are broadly used for the design and analysis of adaptive, intelligent systems for a number of reasons. These networks are also able to recognize spatial, temporal or other relationships and performing tasks such as classification, prediction and function estimation.

4.5 NEURAL NETWORK AS A PATTERN RECOGNISER

A neural network is a massively parallel distributed processor which is made up of simple processing units, having a natural property for storing experiential knowledge and making it available for use. It resembles the brain in two respects:

1. Knowledge is gained by the network from its environment through a learning process.
2. Interneuron connection strengths which is known as synaptic weights, are used to store the acquired Knowledge."

The artificial neuron is the heart of every neural network. It receives input signals, xi , from n number of neurons and aggregates them by using the synaptic weights, wi . Finally, it passes the result after suitable transformation (transfer function) as the output signal yi. Important transfer functions are given in Figure7. These individual neurons are accumulated to layers.

A general neural network consists of following layers –

1. input layer,
2. one or more hidden layer(s)
3. output layer.

These layers are generally fully connected. Neural network learning algorithms can be classified into supervised and unsupervised:

1. Supervised neural networks need an external "teacher" during the learning phase, which goes before the recalling (utilization) phase.
2. Unsupervised neural networks "learn" from correlations of the input. Neural networks are used for regression and classification. In regression, the outputs present some desired, repeatedly valued transformation of the input patterns. In categorization the objective is to assign the input patterns to one of various categories or classes, usually presented by outputs restricted to lie in the range from 0 to 1, so that they represent the probability of class membership. Pattern recognition is defined as the process whereby a received pattern or signal is assigned to one of prescribed number of classes. Pattern recognition performed by neural network is statistical, with the patterns being presented by points in multi dimensional decision space. The decision space is divided into regions, each one of which is associated with category. The decisions are determined by the training process[5].

5. DEVELOPMENT OF ELECTRONIC NOSE

The Electronic Nose can be categorized into three Generations starting from its development in the mid 80's.

5.1. The First Generation E-Nose

The first generation of e-nose was based on Sensor Arrays (with various types of sensors).

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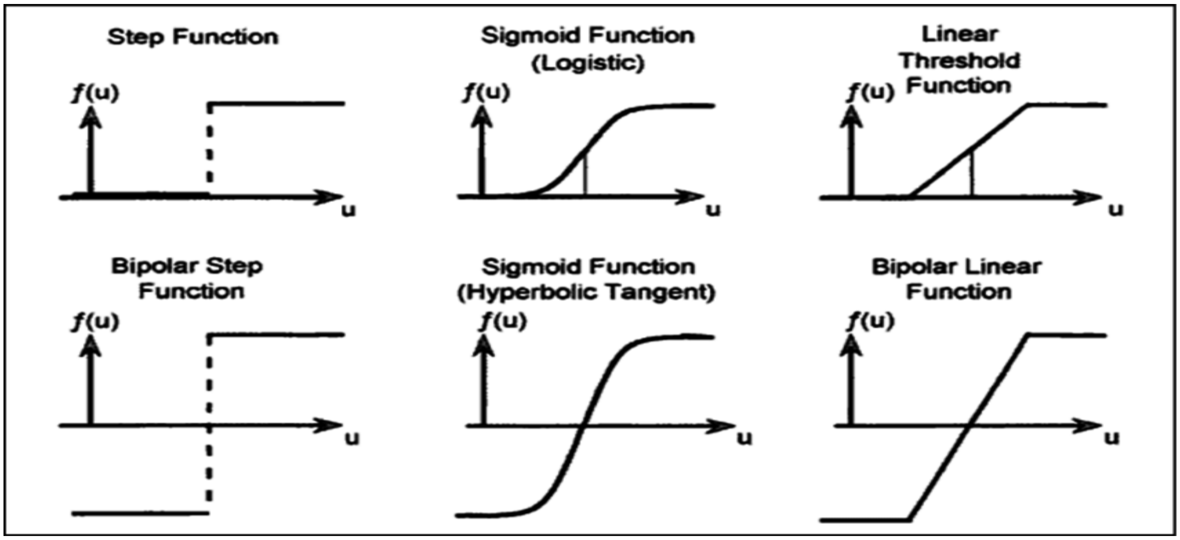
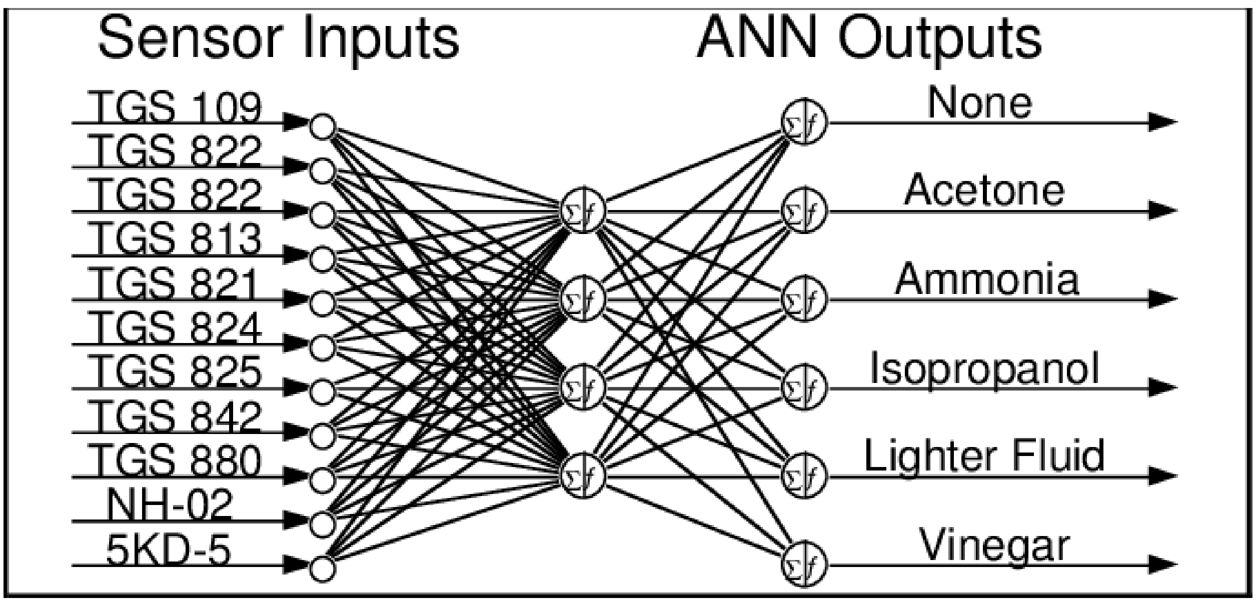


Fig.7. Transfer Function



ig.8: Artificial Neural Network

The 1st generation E-Nose Sensor Unit flight experiment, which flew aboard the STS-95 (1998), used an HP-200LX Palmtop Computer for device monitoring and data acquisition; data were collected and analyzed after landing.

5.2. Second Generation E-Nose

The second-generation E-nose (Figure 5) has the similar functions as the first-generation device, but has been miniaturized to take up less than 1000 cm3 with a mass ~800 g, not including the operating computer.

Fig.9: First Generation E-nose

The power requirements of the 2nd -generation E-nose are same to those of the 1st generation device. The body and flow system of the 2nd generation device are made from a single block of hard-anodized aluminum; the design was chosen to remove fittings and to ensure that no leaks are there in the flow system. Development of the second generation E-nose for crew quarters air quality controlling, emphasizes on optimizing the response of the array of conduct metric sensors and on large ground testing. The sensors are films of polymers which have been loaded with carbon to make them conductive. After the E-nose Flight Experiment on STS-95, it was clear that confidence in the ability of E-nose to identify, and quantify compounds cannot be developed during flight. Such confidence should be developed on the ground, with an optimized device and testing conditions which will challenge the sensors and the recognition software. Sensor optimization work has included studies of noise, reaction time, and sensor recovery by studies of conductive medium, film thickness and sensor size. Data acquisition work has focused on the use of AC measurements of the sensor response to ppm levels of contaminant. AC methods may allow the use of very thin films and thus increase sensitivity while decreasing noise.The sensor, a film of carbon-loaded polyethylene oxide, responds to an injection of 4700 ppm ethanol. The objective of this project is to prepare the E-nose Sensor Unit as a technology demonstration on board the International Space Station (ISS). A modified 2nd Generation E-nose Sensor Unit coupled with an Interface Unit will become the 3rd Generation E-nose.

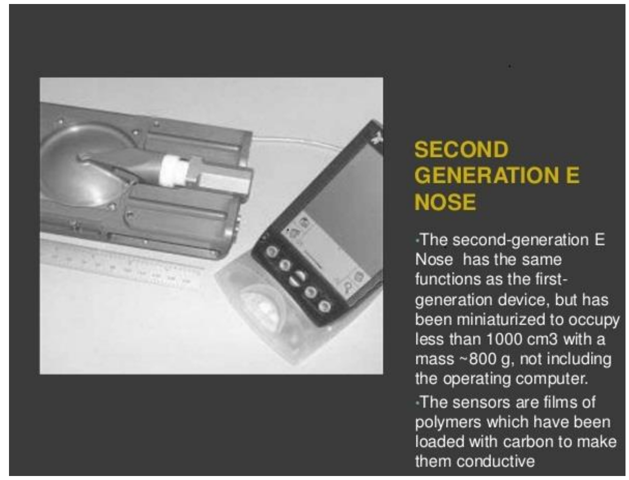


Fig.10: Second Generation E-Nose

5.3 Third Generation E-Nose

The 3rd generation E-nose uses the fundamental sensing unit developed as the second generation device; this also includes an ISS interface unit that conforms to electrical, data telemetry, display and data storage requirements for ISS. The E-nose Sensor Unit includes of an anodized aluminum chassis which houses the Sensor array and pneumatic system. The E-nose Sensor Unit also consists the electronics to route power, relay data and commands between the Sensor array and the E-nose Interface Unit.

The ISS computer system manages dataset collection from the E-nose Sensor Unit and communication between the ISS and the E-nose Unit. A data analysis computer will also be used inside the E-nose Interface Unit. The E-nose Interface Unit will monitor the thermal environment of the E-nose Sensor Unit.

6. APPLICATIONS

Harnessing E-nose technology finds application over vast spectrum of fields, ranging from food to modern medicine (Dickinson 1998).

6.1. Non-Medical Applications

With advancement in this technology, number of applications have been grown such as devices to replace sniffer dogs in Defense department (Schmiedeskamp 2001), to check the quality of , ripeness of fruit quality, food, beverage product certifications in food industry (Mielle 1996, Sameer

1996, Schaller 1998, Ritaban 2003, Xiaobo 2003, Benedetti 2004, Canhoto 2005, Casalinuovo 2005, Casalinuovo 2006, Lozano 2006, Nicolas 2006) and for environmental monitoring such as detecting hazardous chemicals like Nitrobenzene (Diana 1995, Baby 2000, Bancha 2002, Persaud 2005 b, Emmanuel 2006). It is also used for the process monitoring in quality check in industrial production and to diagnose hazardous compounds monitoring for people safety.

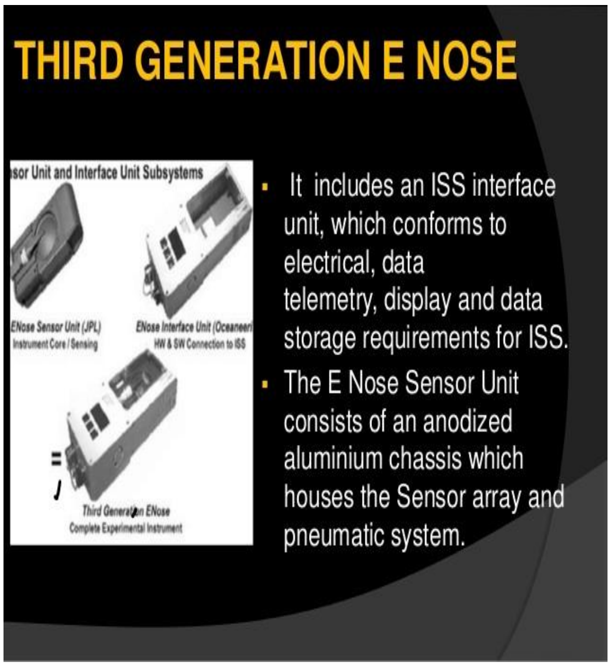


Fig.11: Third Generation E-Nose

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6.2. Medical Applications

One of the major applications emerging today out of E-nose system is in the medical arena for diagnosis. It is not yet been commercialized but still showing great results in research. As the sense of smell is an important sense to the physician, E-nose is capable of being a diagnostic tool. With E-nose both infectious and non infectious diseases can be detected. It has also been proved that E-nose can be used for detecting TB, Diabetes, Gastro esophageal disease, Pneumonia, general illness, etc. (Gibson 2000, Pavlou 2000 b, Ritaban 2002, Parry 1995, Pavlou 2004, Thaller 2005, Di Natale 2000). They also show great results in detecting lung cancers (Di Natale 2003, Hao 2003, Xing 2005, Chan 2009). Recently, a conducting polymer sensor array based E-nose was applied successfully to monitor hemodialysis (Di Natele 1999, Yuh-Jiuan 2001, Fend 2004). Silvano et al (2007) predicted asthma using E-nose. Brisk diabetic diagnosis was also made possible by this technology (Ping 1997, Mohamed 2002).

6.3. COMMERCIAL ELECTRONIC NOSE

In 1964, Wilkins and Hatman made an effort to mimic human nose (Gardner 1994). However in 1987, the first E-nose, as an intelligent system, was developed by Persaud and Dodd at Warwick University (Gibson 2000). The first commercial E-nose was invented in the early 1990s (Gibson 2000). Today, many commercial E-noses are available in the market [6].

Conclusion

A universal electronic nose able of recognizing or discriminating any gas template type with high efficiency and for all possible applications has not as yet been built. This fact is largely due to the selectivity and sensitivity limitations of e-nose sensor arrays for particular analyte gases. Electronic noses are not created to be universally appropriate sensor systems for every conceivable gas-sensing application not are they capable of serving every possible analytical use. Thus, the appropriateness of an electronic nose for a specific application is highly dependent on the required operating conditions of this sensor in the array and the combination of the analyte gases being detected. A exact selection of an accurate e-nose system for a specific application must involve an determination of systems on a case by case basis. Some key considerations indulge in e-nose selection for a specific application must necessarily include assessments of the selectivity and sensitivity range of individual sensor arrays for particular target analyte gases (likely present in samples to be analyzed), the number of unnecessary verbosity suitability sensors with equal sensitivities, and several operational requirements such as run speed or cycle time, recovery time duration between samples, dataset analysis and result-interpretation requirements.

Acknowledgement

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